Thermal Decomposition Approach for PETN Detection in Improvised Explosive Devices

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Abstract- **Pentaerithytol tertranitrate (PETN) is a secondary high explosive primarily used for military and industrial applications. However, it also finds its way into illegally made or obtained Improvised Explosive Devices used for terrorist and Naxal activities. Forensic analysis becomes important in cases when explosions are suspected to be caused by PETN containing explosive compositions. Analysis of PETN is easy when methods such as Colour tests, Thin Layer Chromatography, HPLC, Infrared Spectroscopy, UV-Visible Spectroscopy are used. However analysis by techniques using high temperatures such as Gas Chromatography and Mass Spectrometry does not yield results of great use as PETN is a thermally labile compound. Numerous previous works have developed methods on GC, MS and GC-MS systems which require special equipment and devices. Our work presents a method of detecting the presence of PETN using the CG-MS method with standard column and mass spectrometer parameters without using such special equipment and devices based on the study of breakdown products of intact PETN molecules.**

Keywords: **PETN, Secondary High Explosive, Gas Chromatography Mass spectrometry, Improvised explosives, Military Explosive.**

I. INTRODUCTION

Explosives which are caused to detonate are called as high explosives. They create shock waves, cause effects on surroundings such as bursting, shattering, penetrating, lifting and heaving objects and creating an air blast [1]. Pentaerythritol tetranitrate (PETN), is a high explosive of organic nature belonging to the nitrate ester family, same chemical family as that of nitroglycerin (NG) and nitrocellulose (NC) [2].

PETN is one of the most powerful and most brisant explosives, with satisfactory Stability and moderate Sensitivity. PETN can also be incorporated into gelatinous, industrial explosives [3]. It is the most stable and least reactive of the common nitrate ester explosives [4]. This is attributed to the symmetry in the structure of the PETN molecules [5]. The relatively high sensitivity of PETN to friction and impact requires desensitization with phlegmatizers. In this form it is used in detonation cord, boosters and as a base charge in detonators. It is used as a high explosive due to its physical, chemical and explosive properties [4]. These properties also make PETN favourable to be used in terrorist and naxalite activities in the form of detonating cords, detonators, boosters, blasting agents [6,7]. Hence, forensic analysis and detection of PETN from pre and post blast residues becomes significant as it helps to identify the explosive and connect the type of explosive to the culprits. [8]

Forensic science laboratories receive three types of samples in connection to an explosive case, namely, unexploded bulk samples, post-blast debris and swab materials taken from immovable surfaces or non-transportable bulk objects from the blast site [2]. Post blast Exhibits may contain unexploded residues from the explosive composition. During explosion some portion of explosive material vaporises due to heat and later settles on the colder parts near the seat of explosion. [7] Proper extraction and analysis of this unexploded residue can lead the investigating agencies to the identity of the explosive substance used and further to the culprits.[8]

Analysis of exhibits in high explosive cases entails meticulous extraction procedures ensuring maximum recovery of target compound from the bulk unexploded explosive compositions or post blast debris [9]. Detection and identification of explosives is a difficult task because of thermal stability issues of explosives and the high sensitivity required of analytical techniques.[8] Although explosives are thermally unstable, GC is a good method for separation and identification of explosives.[8]

However, it can be difficult to analyse PETN due to its low vapour pressure and its thermal lability. Hence, a vapour density of a pure substance cannot be maintained, such as needed by GC analysis. Attempts to rise the vapour pressure using higher temperatures cause degradation of the PETN molecules due to its thermo-labile nature. Decomposition is appreciable at temperatures above 100ºC [10, 6]. This leads to degradation of the PETN molecules at high temperatures that are usually used for GC and MS analysis. [11-15]. This complication doesn't allow use of Gas chromatographic methods for analysis of PETN in comparison to other methods of analysis which don't use high temperatures. This has led to many works altering the normal parameters of GC analysis to make them suitable for PETN analysis. Experimental conditions were changed using a considerably shorter GC capillary column of 1.5 meters instead of 15 meter conventional column for avoiding PETN degradation in long GC column.[16].

Another difficulty noted is that of the similarity in the EI mass spectra of explosives group- nitrate asters, like PETN and NG. The EI mass spectra for the two compounds are not unique and show no molecular ion peaks [17]. Sole reliance on Mass spectrometer (MS) analysis un-reliable for detection of Nitrate esters group of explosives. Thus it is necessary to use GC along with MS for confirmatory analysis of such explosives using Retention Time (RT) of Standard substances for comparison. Techniques using FAPA ionisation method coupled to HRMS have been used as an alternative detection method to reduce the fragmentation in comparison to electron ionisation [16]. A method using ion trap mass spectrometer with direct infusion electrospray ionisation was used to detect PETN molecule as adduct with format ions [18].

This work presents a solution to the above-mentioned problems. It makes use of gas chromatography coupled with mass spectrometry method (GC-MS) with all ordinary parameters for analysis of PETN sample. This PETN sample was characterised previously using colour test and FTIR methods. This characterised sample was then used to develop a GC-MS method for PETN based on the study of temperature degradation pattern of the PETN from literature. This method makes use of an easily available instrumental technique requiring no special treatment for sample preparation. The parameters like ionisation techniques, column length, and detection method are that of a conventional GC-MS instrument widely available in any forensic laboratory. As it is not economical and feasible to have special instruments for each and every compound's analysis in a forensic laboratory, this method presents a novel and different way of analysing PETN from its degradation product from the GC instrument and further identification of this degradation product using Mass spectrometer. This solves another problem associated with PETN analysis because although the mass spectra for nitrate esters is similar, it is dissimilar for the PETN fragments obtained using the methods developed in our work. In this way our work utilises the thermo-labile nature of the PETN molecule for its confirmation in indirect manner based on its degradation products.

II. MATERIAL AND METHODS

2.1. Chemicals Required, Regents & Sample Preparation

PETN sample was obtained from a case sample and characterised using Diphenylamine colour test and FTIR Analysis. Acetone (AR) was obtained from Advent Chembio Pvt. Ltd. for preparing 100ppm solution of PETN. One gram Diphenylamine (Extra pure AR grade) from Sisco Research Laboratries Pvt. Ltd. was dissolved in 10 millilitres (ml) concentrated Sulphuric Acid from Sigma Aldrich (Switzerland) to prepare reagent for performing colour test.

2.2. Instrumentation

Fourier Transform Infra Red (FTIR) analysis was performed on a Thermo Fisher Scienific Nicolet iS20 FTIR spectrometer instrument with Attenuated Total Reflectance (ATR) accessory from Thermo Fisher Scientific using software Thermo Scientific OMNIC. The sample was scanned 64 times at resolution of 4.000 using DTGS detector and KBr beam splitter between 4000.12 cm^{-1} to 525.03 cm^{-1}.

GCMS analysis was performed on Thermo Scientific TRACE 1600 Gas Chromatograph mounted with Thermo Scientific AI/AS 1610 Auto sampler coupled with Thermo Scientific ISQ 7610 MS mass spectrometer as detector. Column used for separation was Thermo Scientific TG-5MS of length 30 metres, I.d. 0.25mm and film thickness 0.25 micron using helium as carrier gas. Five different GC-MS methods were optimised for obtaining least degradation as possible. The mass spectra of the degradation products and it's similarity with the mass spectra of the PETN were studied. The details of the instrument methods used are given in table 1.

Table 1: Details of the instrument methods

		INSTRUMNT MTHODS				
		HE-1	HE-2	HE-3	HE-4	HE-5
MS PARAMTRS	Ion polarity	Positive	Positive	Positive	Positive	Positive
	Start mass [amu]	30	30	30	30	30
	End mass [amu]	500	500	500	500	500
	Scan time [sec]	0.2	0.2	0.2	0.2	0.2
	MS transfer line temperature	175 °C	180 °C	160 °C	165 °C	165 °C
	Ion source temperature	150 °C	150 °C	150 °C	150 °C	150 °C
	Ionization mode	EI	EI	EI	EI	EI
	Start time	3.2 min	3.2 min	3.2 min	3.2 min	3.2 min
GC PARAMTRS	Run time [min]	18.333	17.250	14.667	11.143	10.168
	Inlet Temperature	145 °C	175 °C	160 °C	160 °C	150 °C
	Column Description	"TG-5MS"	"TG-5MS"	"TG-5MS"	"TG-5MS"	"TG-5MS"
	Column Length [m]	30.00	30.00	30.00	30.00	30.00
	Nominal ID [mm]	0.250	0.250	0.250	0.250	0.250
	Film Thickness [µm]	0.25	0.25	0.25	0.25	0.25
	Carrier Flow [ml/min]	1.000	1.000	1.000	1.000	1.000
	GC Oven Temperature Nominal	Start at 50.0 [°C] no hold	Start at 50.0 [°C] hold for 1.0 min	Start at 50.0 [°C] hold for 1.0 min	Start at 50.0 [°C] hold for 1.0 min	Start at 50.0 [°C] hold for 1.0 min
		Ramp from 50.0 [°C] to 175 [°C] at 15 [°C]/min	Ramp from 50.0 [°C] to 175 [°C] at 20 [°C]/min	Ramp from 50.0 [°C] to 160 [°C] at 30 [°C]/min	Ramp from 50.0 [°C] to 160 [°C] at 35 [°C]/min	Ramp from 50.0 [°C] to 100 [°C] at 30 [°C]/min
		Hold for 10 min at 175 [°C]	Hold for 10 min at 175 [°C]	Hold for 10 min at 160 [°C]	Hold for 1 min at 160 [°C]	Hold for 1 min at 100 [°C]
					Ramp from 160.0 [°C] to 165 [°C] at 1 [°C]/min	Ramp from 100.0 [°C] to 150 [°C] at 20 [°C]/min
					Hold for 1 min at 165 [°C]	Ramp from 150.0 [°C] to 165 [°C] at 5 [°C]/min
						Hold for 1 min at 165 [°C]

Amu-atomic mass unit, sec-second, °C- degree Celsius, min-minutes, m-metre, mm-milli metre, µm-micro metre.

The method design was based on study of temperature profiles of PETN at different temperatures [16]. In no method, temperatures higher than 175 °C was employed to avoid thermal degradation of PETN [7,19].

III.RESULTS AND DISCUSSION

3.1. Characterisation of PETN Sample

Colour test was performed on a ceramic spot plate by adding one drop of reagent to one drop of PETN solution. Diphenylamine reagent gave a deep blue colouration indicating presence of PETN in the case sample [20]. FTIR analysis of PETN sample was carried out using ATR FTIR assembly by scanning background and sample. It gave characteristic FTIR spectrum of PETN with 90.22% match probability with PETN Diamond ATR on performing a library search using correlation search type, as shown in fig. 1, thus confirming presence of PETN in the given sample.

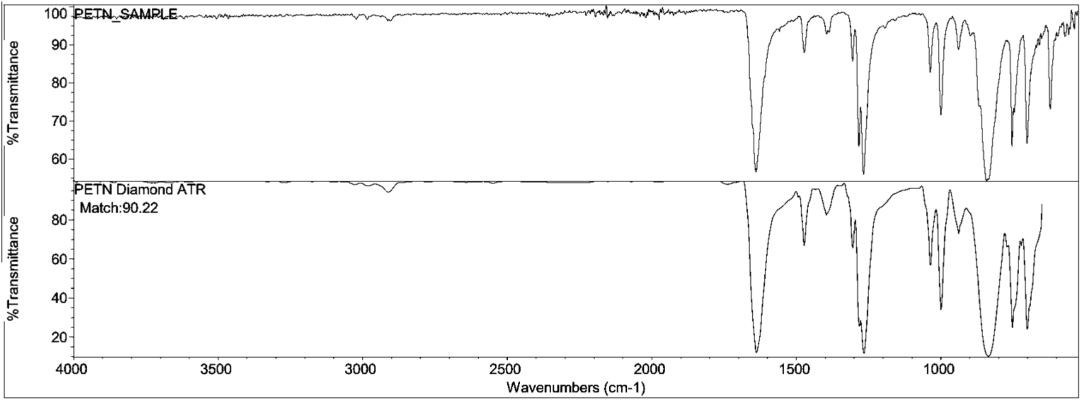
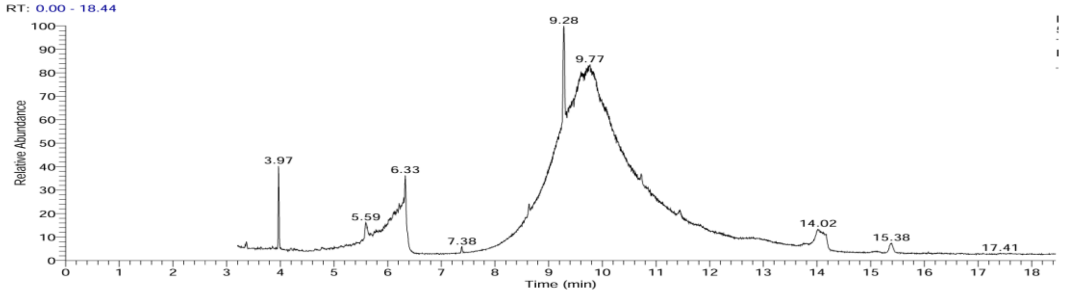


Fig.1. FTIR spectrum of PETN sample (top) and FTIR spectrum of PETN diamond ATR from Library match (bottom)

3.2. Gas Chromatography Mass spectrometer

The Total Ion Chromatogram (TIC) of PETN sample obtained using five instrumentation methods HE-1 to HE-5 and details of the relevant degradation product detected at various Retention time (RT) are given below in Figs. 2 to 6.



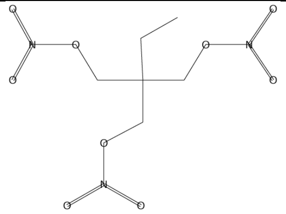
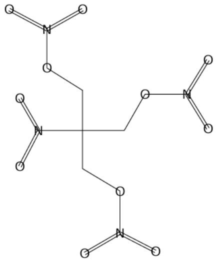
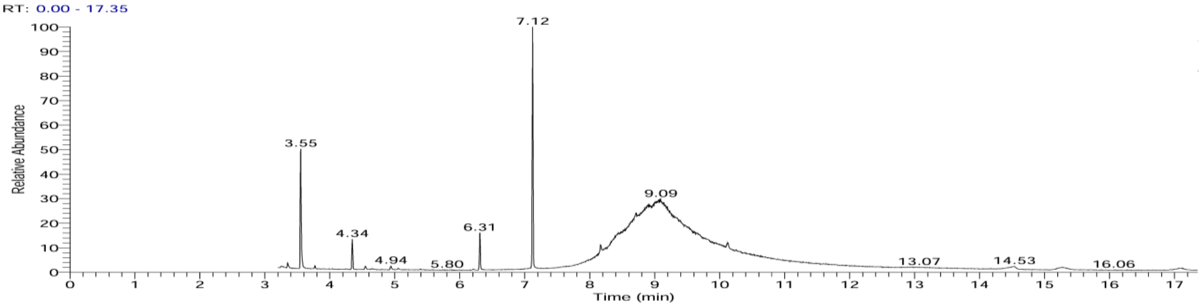
	RT	5.59	COMPUND STRUCTURE
a	Compound name	2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate	
	Formula	C6H11N3O9	
	Molecular weight	269	
	Top five mass peaks	46, 30, 43, 55, 76	
b	RT	8.63	
	Compound name	Nitroisobutanetriol trinitrate	
	Formula	C4H6N4O11	
	Molecular weight	286	
	Top five mass peaks	46, 30, 43, 56, 76	

Fig. 2. TIC obtained from method HE-1 (TOP) and details of compound detected (a,b)



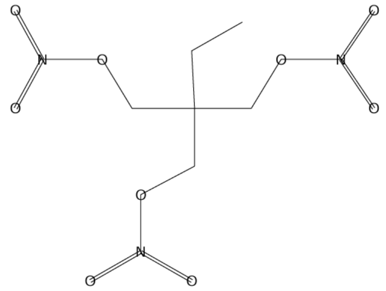
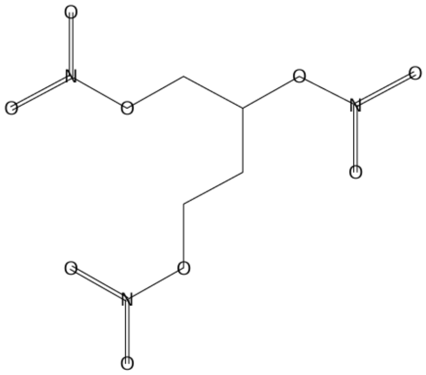
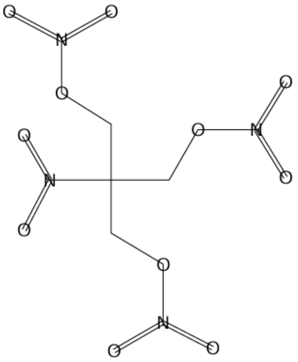
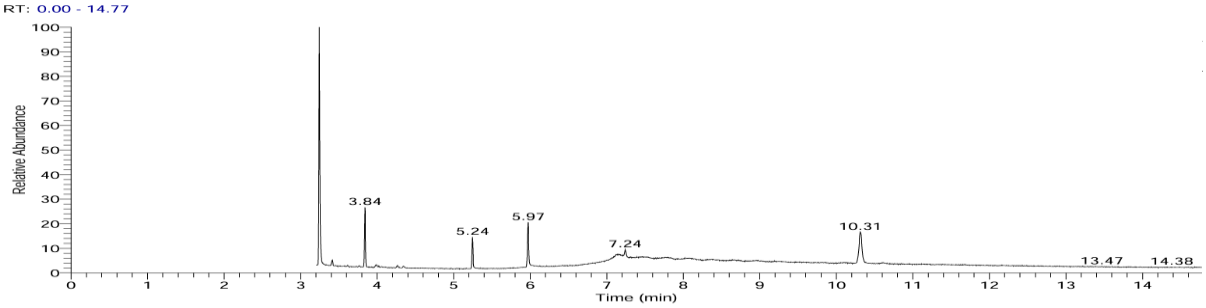
	RT	6.31, 8.17, 14.53	COMPUND STRUCTURE
a	Compound name	2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate	
	Formula	$C_6H_{11}N_3O_9$	
	Molecular weight	269	
	Top five mass peaks	46, 30, 43, 55, 76	
b	RT	8.71	
	Compound name	1,2,4-Butanetriol, trinitrate	
	Formula	$C_4H_7N_3O_9$	
	Molecular weight	241	
	Top five mass peaks	30, 46, 42, 57, 60	
c	RT	9.06, 10.12	
	Compound name	Nitroisobutanetriol trinitrate	
	Formula	$C_4H_6N_4O_{11}$	
	Molecular weight	286	
	Top five mass peaks	46, 30, 43, 56, 76	

Fig. 3 TIC obtained from method HE-2 (TOP) and details of compound detected (a,b.c)



a	RT	5.97, 7.15, 7.24
	Compound name	Nitroisobutanetriol trinitrate
	Formula	C4H6N4O11
	Molecular weight	286
	Top five mass peaks	46, 30, 43, 56, 76

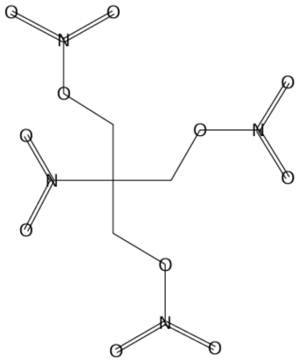
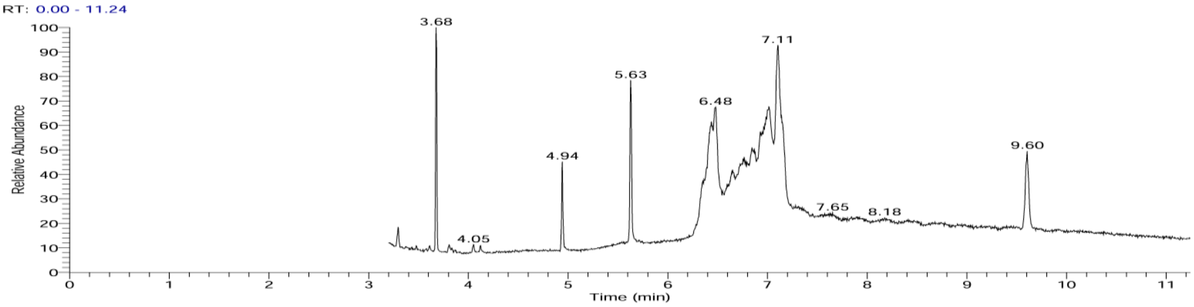
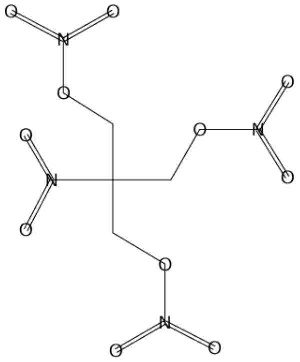


Fig. 4 TIC obtained from method HE-3 (TOP) and details of compound detected (a)



a	RT	6.55, 6.64, 6.77, 6.84, 7.31, 7.46, 7.84, 7.89, 8.18, 8.40, 8.47, 8.74, 8.98, 9.15, 10.14
	Compound name	Nitroisobutanetriol trinitrate
	Formula	C4H6N4O11
	Molecular weight	286
	Top five mass peaks	46, 30, 43, 56, 76



b	RT	9.60
	Compound name	2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate
	Formula	C6H11N3O9
	Molecular weight	269
	Top five mass peaks	46, 30, 43, 55, 76

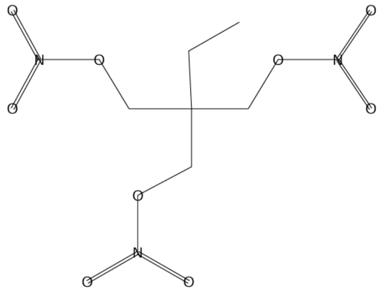
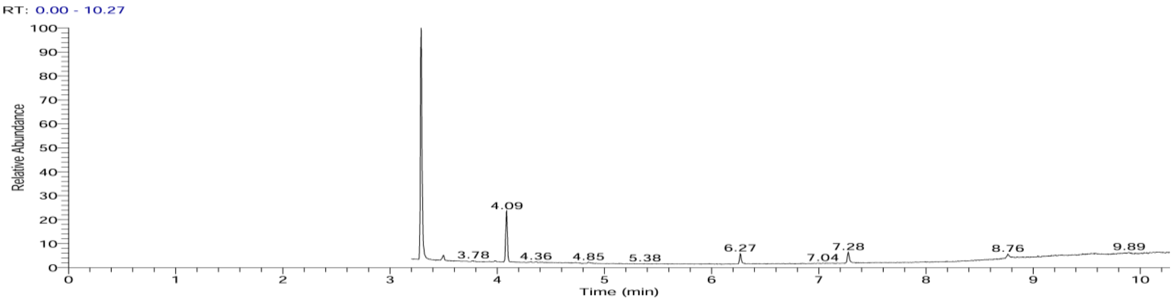


Fig. 5 TIC obtained from method HE-4 (TOP) and details of compound detected (a,b)



a	RT	8.76

Compound name	2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate
Formula	$C_6H_{11}N_3O_9$
Molecular weight	269
Top five mass peaks	46, 30, 43, 55, 76

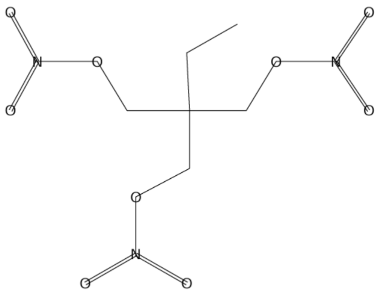
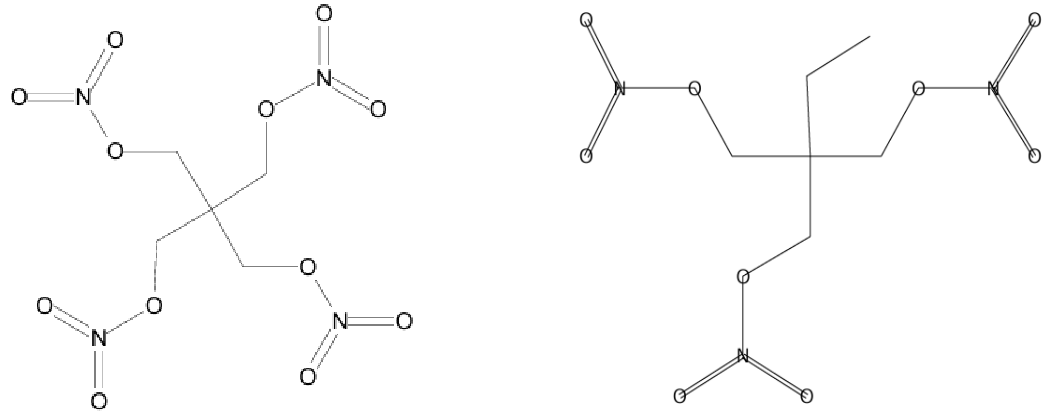


Fig. 6 TIC obtained from method HE-5 (TOP) and details of compound detected (a)

The GC-MS analysis detected the compounds which were similar in structure to PETN, namely, 2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate, Nitroisobutanetriol trinitrate and 1,2,4-Butanetriol, trinitrate. Of these structures, 2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate was detected in all except one method HE-3. Method HE-2 could detect three degradation products. HE-3 and HE-5 could detect only one degradation product each, Nitroisobutanetriol trinitrate and 2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate respectively. HE-1 and HE-4 methods could detect only two degradation products, 2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate and Nitroisobutanetriol trinitrate. 1,2,4-Butanetriol, trinitrate could be detect only in one method HE-2. Molecular structures of these three degradation products and PETN molecule are given in fig. 7.

(a) Pentaerythritol Tetranitrate (MW 316)

(b) 2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate (MW 269)



(c) Nitroisobutanetriol trinitrate (MW 286)

(d) 1,2,4-Butanetriol, trinitrate (MW 241)

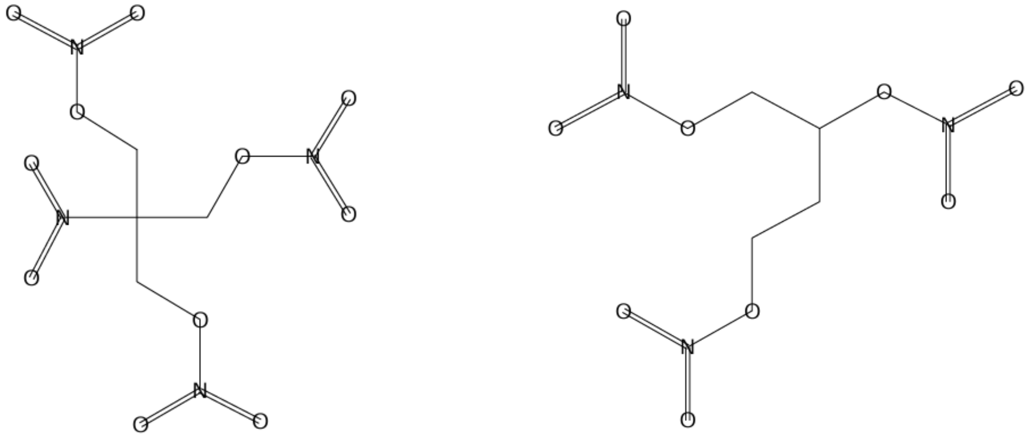


Fig. 7 Structures of PETN and its degradation products

Comparative molecular structure and EI mass spectra of PETN and Nitroglycrine (NG) from a previous work are given in fig. 8 [17]. It can be seen in fig 8, that mass to charge (M/Z) values are almost same for both the compounds, PETN and NG without any molecular ions peaks. Figs. 9, 10 and 11 show the mass spectra of the degradation products. Here also it can be seen that no molecular ion peaks are seen for the degraded product. M/Z values of 30, 46 and 76 which are seen in mass spectrum of PETN are also seen in the mass spectra of the degradation products along with many other distinguishing M/Z values.

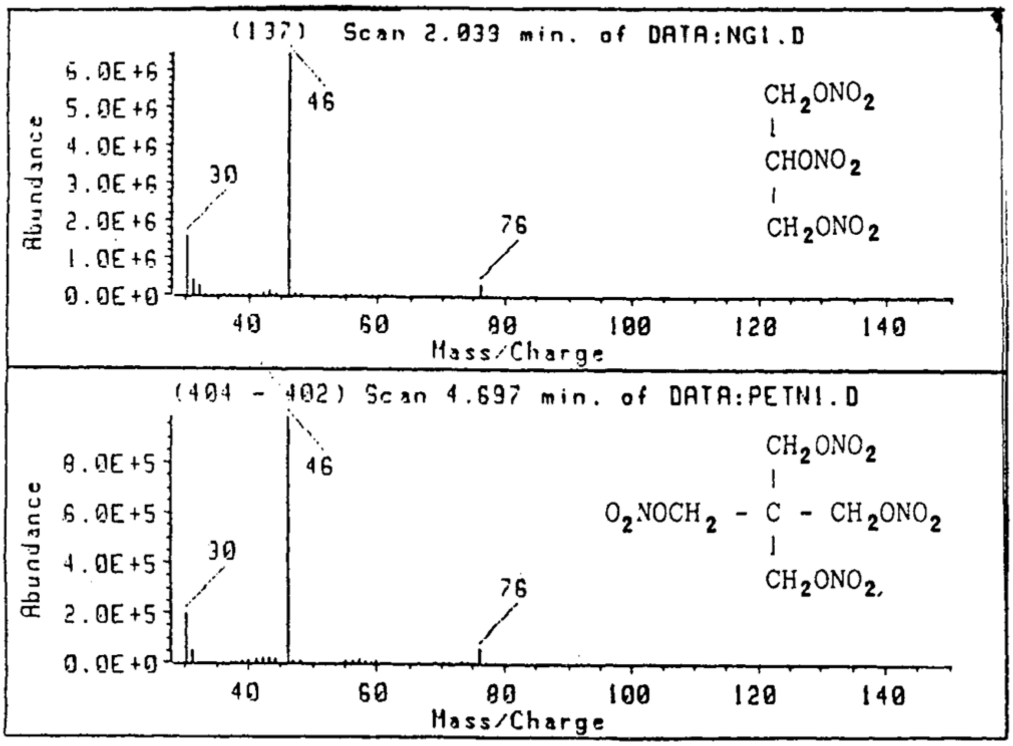


Fig. 8 EI Mass Spectra of NG and PETN [17]

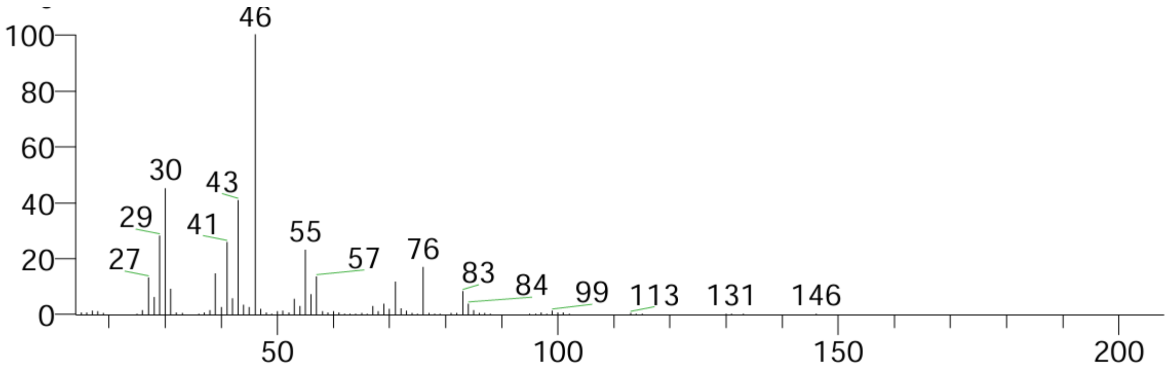


Fig. 9. EI Mass Spectra of 2-Ethyl-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate (MW 269)

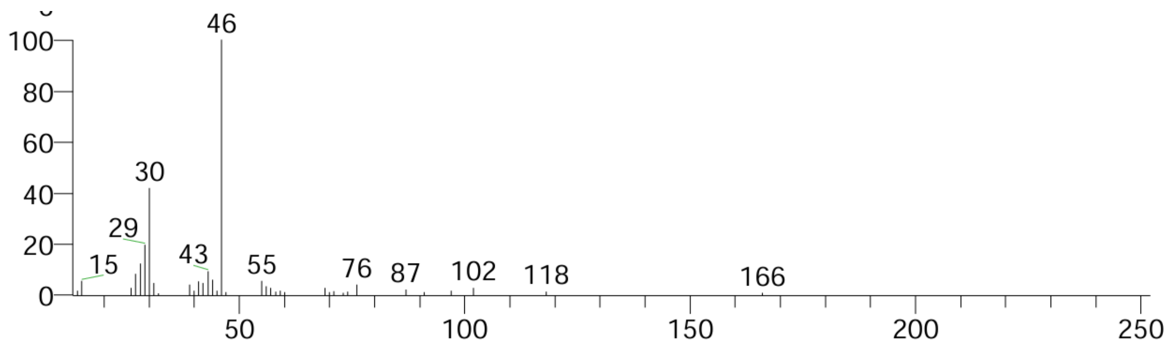


Fig. 10. EI Mass Spectra of Nitroisobutanetriol trinitrate (MW 286)

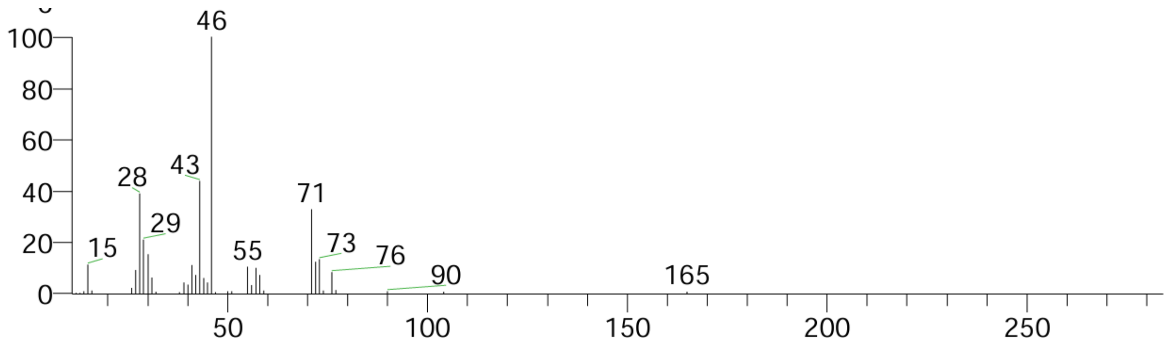


Fig. 11. EI Mass Spectra of 1,2,4-Butanetriol, trinitrate (MW 241)

IV.CONCLUSIONS

Mass spectra of two nitrate esters NG and PETN show similar M/Z values thus not allowing conclusive detection of explosive compounds of similar nature [17]. Hence further study of these compounds can be based on the breakdown products of these compounds.

M/Z values of 30 (NO^+), 46 (NO_2^+) and 76 ($CH_2ONO_2^+$) are common to the PETN molecule and the degradation product molecules indicating that they are structurally similar. Structural similarity points towards fact that these detected compounds are degradation products of PETN. Study of fig 7 (a), (b), (c) and (d) shows that degradation products are formed by loss of small molecular moiety with subsequent addition or rearrangement within the molecules.

Lack of molecular ion peaks in the mass spectra of degradation products indicates that the degradation products also undergo higher degree of fragmentation at the Electron ion source. Thus mass spectra of degradation products of PETN also don't show any molecular ion peaks.

The distinguishing M/Z values (apart from M/Z values of 30, 46 and 76) of degradation products are a better means to detect presence of PETN degradation products, and indirectly to detect PETN, as these values will neither be obtained in the mass spectra of other nitrate ester explosives nor in the mass spectra of their degradation products.

Method HE-2 detected three such degradation products and hence appears to be better than other methods that could detect either two or only one product. However, the TIC of samples run using methods HE-1, HE-2 and HE-4 show many unresolved peaks, which may be resolved with better temperature programming. Thus we must consider the two methods HE-3 and HE-5. These two methods show good peak resolution. The molecular structure obtained from method HE-3 is more similar with structure of PETN [(a) and (c) in Fig.7] and it is just 30 mass units less than PETN due to loss of –[CH_2 – O]– moiety. The method HE-3 may be considered as suitable method among the five.

Abbreviation:
PETN -Penta erythritol tetranitrate,
HPLC - High performance liquid chromatography
UV - Ultra violet, CG - Gas chromatography,
MS - Mass spectrometry, GC- MS Gas Chromatography Mass spectrometry
NG - Nitro glycerine
HRMS - High resolution mass spectrometry
FAPA - Flowing atmospheric-pressure afterglow
AR - Analytical reagent
Pvt. - Private
Ltd. - Limited
FTIR - Fourier Transform Infra Red spectroscopy
ATR - Attenuated Total reflectance
DTGS - Deuterated Triglycine Sulfate
HE - High explosive
ID - Inner diameter
TIC - Total ion chromatogram
MW - Molecular weight
RT - Retention time
EI - Electron ionisation
M/Z - Mass to charge

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